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# FINAL REPORT

## The Fate and Transport of Perchlorate in a Contaminated Site in the Las Vegas Valley

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# *EXECUTIVE SUMMARY*

## Introduction and Research Objectives

The research reported herein represents a multidisciplinary investigation involving several aspects of extreme perchlorate contamination in the Basic Management Industrial (BMI) complex in Henderson, Nevada. Perchlorate ($ClO_4^-$), an important component of rocket fuel and explosives, has been detected in several water supplies throughout the United States. Perchlorate interferes with iodide uptake into the thyroid gland disrupting the production of the thyroid hormones that help regulate metabolism and in children, also plays a vital role in proper development. There is currently no set maximum contaminant level (MCL) for perchlorate in drinking water. However, in January 2002, the US Environmental Protection Agency (USEPA) published a draft risk assessment of perchlorate proposing a drinking water level of 1 ppb (part per billion) for perchlorate.

Perchlorate has being produced and handled in Henderson, NV, in the BMI complex since the early 1940's. The two perchlorate-manufacturing facilities located in Henderson, the Kerr-McGee and the PEPCON plants, supplied the entire perchlorate demand for the United States until 1988, when the PEPCON plant was destroyed by an explosion. From the early 1940's to 1976, perchlorate was released to the environment by leaks in the industrial plants and storage ponds and by the disposal of perchlorate containing wastes into unlined ponds. As a result of continuous percolation of perchlorate-containing wastes the near surface aquifer was contaminated. The contaminated groundwater then seeped into the Las Vegas Wash, located approximately 3 miles from the industrial site, reaching Lake Mead and the Colorado River. The Colorado is the water source for millions of people in Nevada, Arizona and California. Lake Mead is the main water supply for the 1.3 million residents of the Las Vegas Valley.

This research examines the extent of perchlorate interaction with various environmental components and their effects on the fate and migration of perchlorate in the surface and subsurface in the highly contaminated site in Henderson. The specific objectives of the research were:

A. To model the subsurface transport of perchlorate from the contaminated site to the Las Vegas Wash,
B. To investigate the role of indigenous microbial communities on the biodegradation of perchlorate in the site, and
C. To evaluate the influence of soil sorption on the migration of perchlorate and assess the potential of chemical (abiotic) reduction of perchlorate in the contaminated site.

This report contains three parts: **Part A** presents the groundwater transport model of perchlorate from the contaminated site to the Las Vegas Wash. It contains information on the number of perchlorate-contaminated plumes, times of travel for perchlorate from the various plumes to the Wash, and an estimation of the plume volumes and amount of perchlorate contained in the contaminated groundwater. **Part B** examines the potential for natural biodegradation of perchlorate in Las Vegas Wash area and Lake Mead. It includes enumeration, isolation, and characterization of indigenous perchlorate reducing microorganisms, microcosm testing, current and historical perchlorate concentration distributions in the Las Vegas Wash, and seasonal perchlorate levels variation in Lake Mead. **Part C** comprises investigations of the interactions of soils and sediments with perchlorate in the contaminated site. It contains the concentrations of perchlorate in sediments along the Wash and in the contaminated site, and column test results on the retardation of perchlorate in different soils and sediments from the site.

The results of this research provide significant information to regulatory agencies, private firms, and decision-makers interested in the remediation of the Henderson and other perchlorate-contaminated sites. It also provides information on the relationship between the perchlorate concentration in the Las Vegas Wash and its concentration in Lake Mead and the Colorado River. Following is a summary of the major findings of this research:

## Transport Modeling of Perchlorate in the Contaminated Site

The groundwater in the contaminated site is contained within two distinct sedimentary formations: the top alluvial sediment fan deposits and the upper portion of the underlying Muddy Creek Formation. Groundwater moves faster within the alluvial fan deposits than within the Muddy Creek Formation. The Muddy Creek Formation has very low hydraulic conductivity. Yet, the top of the Muddy Creek Formation contains alluvial channels of high hydraulic conductivity which are preferential pathways for transport to the Las Vegas Wash. The groundwater table is located within the alluvial deposit. However, in the southern portion of the industrial area, the groundwater table is located within the upper portion of the Muddy Creek and transport from the southern portion of the industrial site to Las Vegas Wash is very slow.

Three perchlorate plumes were formed in the contaminated area. The Main plume and PEPCON plumes were formed by perchlorate discharges at the Kerr McGee and the PEPCON industrial sites, respectively. A third plume, the Secondary plume was formed by the disposal of perchlorate-containing wastes into unlined ponds (i.e. the BMI ponds). The Main plume has the highest perchlorate concentrations and moves from the Kerr McGee site down to the Las Vegas Wash. The PEPCON plume has lower concentrations than the Main plume and is present in the vicinity of the former PEPCON plant. The Secondary plume, which contains low perchlorate concentrations, spreads from the BMI Upper Ponds area to the Las Vegas Wash, affecting a large area.

The modeling software MODFLOW and its respective particle-tracking and transport models were used in this research to evaluate both the Main and the Secondary perchlorate plumes in the Henderson site. The PEPCON plume was not considered in the model, due to the lack of data to adequately characterize the site. The results of the particle-tracking model for the Main and Secondary plumes, confirm that perchlorate may have traveled within both, the alluvial deposits and the Upper portion of the Muddy Creek Formation. The results also show that, when traveling within the Muddy Creek, it takes perchlorate longer to reach the Las Vegas Wash than when it travels within the alluvial layer. Furthermore, the results reveal that the pathways of perchlorate transport tend to be controlled by the alluvial channels located on top of the Muddy Creek. The particle-tracking model revealed that perchlorate released in the BMI industrial complex may have taken from 6.6 to 9.6 years to reach the Las Vegas Wash. Perchlorate disposed in the Upper BMI Infiltration ponds may have taken from few months to decades to reach the Las Vegas Wash, depending on the location of the disposal.

The results of the perchlorate transport model confirm that the main plume is directed by a preferential flowpath inside a main alluvial channel. Perchlorate concentration decreases as the main plume moves from the industrial area towards the main alluvial channel. When the main plume reaches the alluvial channel, its concentrations decrease even more and the plume elongates toward the Wash area. The model indicates that high perchlorate concentrations may be predominant in the interface between the top of the Muddy Creek and the alluvial deposits. The evaluation of the time of travel of perchlorate concentration fronts revealed that the 5 ppm and 50 ppm concentration fronts had times of travel, from the industrial area to the Las Vegas Wash, of approximately 25 and 46 years, respectively. This suggests that a clean up of the groundwater in the industrial site, based on self-purging, would take many years.

Simulation for the secondary plume confirms that the perchlorate disposal in the BMI Infiltration ponds affected a large area, despite its lower perchlorate concentrations. The high hydraulic gradients, generated by the industrial wastewater disposal, might have forced perchlorate-contaminated water to migrate down to the Upper portion of the Muddy Creek Formation. The transport of perchlorate through the Muddy Creek may have affected the self-purging time of the secondary plume. Simulation results demonstrate that it took less time for the Secondary Plume to reach the Wash than for the main plume. Most of the secondary plume had been washed out by the year 2001. Domestic and industrial wastewater discharges in the contaminated site decelerated the movement of the main perchlorate plume and contributed to its dilution, decreasing the perchlorate load discharged into the Las Vegas Wash.

The volume and perchlorate mass estimated for the Main plume are 8,679 million gallons (32.8 million $m^3$) and 20.4 million pounds (9,253 metric tons), respectively. For the Secondary plume the estimated volume was 9,032 million gallons (35 million $m^3$) and the estimated perchlorate mass was 1.1 million pounds (498 metric tons). These results indicate that both plumes have approximately the same volume. However, despite its large volume, the secondary plume has a relatively smaller mass of perchlorate, due to its lower concentrations. The main plume contains about 20 times more perchlorate by mass than the secondary plume; that implies the main plume is the major perchlorate source to the Las Vegas Wash. According to this estimate and assuming a withdrawal rate of 1 MGD (694 GPM; 3,785$m^3$/day), the clean- up of the main plume would take approximately 24 years. This estimate implies a removal of approximately 0.86 million ponds (390 metric tons) of perchlorate per year; or more than 2,400 lbs of perchlorate per day.

## Microbiological Investigations

*Perchlorate Distribution and Seasonal Variations in the Wash and Lake Mead*

Analyses of frozen archival water samples from the Las Vegas Wash and Lake Mead reveals that: (a) perchlorate contamination levels in both the Las Vegas Wash and Lake Mead in the 1990's were very similar to today's (2000); (b) the Las Vegas Wash contains very low perchlorate levels (average: 8.8 ppb) upstream of the BMI contaminated site and levels varying from 600-800 ppb downstream from the site; (c) the average perchlorate loading into the Wash varied between 300 to 450 kg/day from 1991 to 2000; (d) statistical analysis of Wash flows and perchlorate loading show that Wash flows significantly affects perchlorate loadings into Lake Mead. Because perchlorate is highly soluble and is present in the Wash sediments and soils from the contaminated site, during high flows (i.e. storm events), it is washed out resulting in high perchlorate loading to Lake Mead and the Colorado; (e) the high perchlorate levels of the Wash (600-800 ppb) are quickly diluted to smaller concentrations after entering the Las Vegas Bay of Lake Mead. The Las Vegas Wash does not mix completely with the Lake's water and perchlorate concentrations in Boulder Basin, where the Wash enters Lake Mead, vary seasonally with Lake stratification. . In Lake Mead, the perchlorate levels within the hypolimnion and metalimnion were significantly higher than those of the epilimnion layers for sampling points close to the Wash. For points further from the Wash (i.e. Hoover Dam outflow), perchlorate levels within the epilimnion layer were higher than those of the hypolimnion; (f) lake stratification significantly affects perchlorate levels at all thermal layers. The epilimnion and metalimnion perchlorate levels during the stratified period were higher than those of the non-stratified period. The hypolimnion perchlorate levels showed exactly the opposite behavior. The increase of the perchlorate levels within the hypolimnion layer during the non-stratified period (that occurs during winter) impact the perchlorate levels in the drinking water intake at Lake Mead. The Las Vegas drinking water supply intake pumps water from the hypolimnion, and therefore, higher perchlorate levels are present in the drinking water during winter; (g) Lake storage level did not seem to have a significant effect on perchlorate levels in the Las Vegas Bay area, but it was found significant for sampling points located further from the Wash entrance.

*Enumeration, isolation, and characterization of Perchlroate-reducing microorganisms*

Enumeration of perchlorate-reducing bacteria in water samples from the Wash and the contaminated site was performed using standard plate count (SPC) and most probable number

(MPN) techniques. Enumeration using the plate count revealed counts varying from $3\times10^3$ to $7.7\times10^4$ counts/ml for the aqueous samples from the Wash and the contaminated groundwater. The enumeration results imply that indigenous perchlorate-respiring microbes are ubiquitous to the Wash site and are present in sufficiently high numbers. The number of perchlorate-reducing microorganisms was found to correlate weakly with the initial perchlorate concentrations in Las Vegas Wash samples. In fact, the smallest counts of indigenous perchlorate degrading microorganisms were found within the Kerr McGee contaminated area, where the perchlorate concentrations are the greatest. Along the Wash, the number of perchlorate-reducing microorganisms was the highest in the immediate proximity of the discharge of the wastewater treatment plant. Most probable numbers for perchlorate-reducing microbes in water samples from the Wash and the contaminated site show a trend similar to that depicted by the SPC counts; with MPN varying from $2.1 \times 10^3$ to $9.2 \times 10^6$ CT/100 ml.

MPN and SPC count in water samples from Lake Mead and soils from the Wash area revealed that the MPN values for Lake Mead water samples ranged from less than 20 to $2.3 \times 10^2$ PRB/100 ml. The SPC values recorded for the water samples ranged from less than 1 to $1.0 \times 10^3$ CFU/ml. When compared to the MPN numbers obtained for aqueous samples from the Las Vegas Wash, the MPN for the Lake Mead water, are four to six orders of magnitude lower. A similar trend was found for standard plate counts; counts in the Wash were two to four order of magnitude larger than in the Lake. Thus, the Las Vegas Wash contains a much larger number of perchlorate-reducing bacteria than Lake Mead. This is not unexpected, since significant dilution occurs when the Las Vegas Wash mixes with Lake Mead. The MPN's recorded for Las Vegas Wash soil samples ranged from less than 20 to greater than $1.6 \times 10^5$ PRB/100 g. SPC values recorded for the soil samples ranged from less than $1.0 \times 10^3$ CFU/g to $5.0 \times 10^6$ CFU/g. These results indicate relatively high number of microbes present in the soils along the Las Vegas, which is a positive asset to potential bioremediation of the contaminated site.

Over thirty strains of perchlorate reducing bacteria were isolated from the contaminated site in this research. Characterization of perchlorate-reducing isolates based on microscopy, morphology, motility, size and colony characteristics show that all strains were motile or hypermotile. Each of the isolates was rod-shaped with cell sizes ranging from (1.0 µm x 3.0 µm) ) to ( 1.5 µm x 7.0 µm), designating width and length, respectively. All strains were catalase and oxidase positive with the exception of one, which was oxidase negative. All isolates were able to utilize a large percent of the 95 electron donors in the BIOLOG™ microplate; 37 - 54% and 28 - 78% for soil and water isolates, respectively. Colony characteristics varied considerably. 16S rDNA sequencing of approximately 550 base pairs revealed that one of the perchlorate-reducing isolates was closely related to the genus, *Dechlorosoma*; several isolates were closely related to different species of the genus, *Aeromonas*; four of the isolates were closely related to the γ-subclass *Proteobacteria*; and two novel perchlorate-reducing strains isolated from Lake Mead waters were closely related to *Shewanella* sp. and *Rahnella aquatilus.*

*Microcosm Testing*

The results of the microcosm studies show that perchlorate biodegradation in the Wash and in the contaminated seepage is electron donor limited. In the absence of an external carbon source, perchlorate biodegradation did not occur. However, when a carbon source was provided, microbial reduction proceeded at fast rates. The BOD of the seepage and of the Las Vegas Wash are very low (1.5 mg/L). Thus, a source of carbon for perchlorate biodegradation is not available to the indigenous perchlorate-reducing microorganisms. In addition to carbon limitation, perchlorate biodegradation in the Las Vegas Wash is limited by the presence of nitrate and oxygen, both of which are preferred electron acceptors to perchlorate. High salinity was also found to negatively influence perchlorate biodegradation in soil and water samples from the contaminated site. It was noticed that perchlorate biodegradation in the sediments samples from the Wash was much faster than that observed in the water microcosms. This may be the result of larger microbial counts for the soils than those for the water samples.

In summary, the results of the microcosm testing indicate that indigenous perchlorate-respiring microorganisms are ubiquitous and numerous in the Las Vegas contaminated site. Natural perchlorate biodegradation in the Las Vegas Wash and the contaminated soils was found to be limited by many factors, including, lack of an electron donor (i.e. carbon source), the presence of high nitrate and oxygen levels in the Wash, and high salinity levels in the contaminated site. However, when a carbon source was provided perchlorate biodegradation proceeded at acceptable rates for areas where the salinity levels were not very high. Therefore, the potential for in situ bioremediation of the sediments along the Wash is high.

### The Role of Soil Sorption and Abiotic Oxidation on the Fate of Perchlorate in the Site

The continuous transport of perchlorate from the contaminated seepage to the Wash has resulted in considerable deposition of perchlorate along the sediments of the Wash. Twenty-seven sediment samples were collected along the Las Vegas Wash. The sediments were characterized and were used in column experiments to assess the migration potential of perchlorate in Las Vegas Wash sediments. The surface area of the sediments was determined by nitrogen adsorption, using the BET model, and by the ethylene glycol monoethyl ether (EGME) method. The two techniques resulted in very similar surface area estimates for some samples, while in other samples the differences were significant, approaching a factor of ten. These differences can be attributed to differences in mineralogy. BET surface areas were high and ranged from 1.5 to 30 $m^2/g$. Mineralogical composition was determined by x-ray diffraction (XRD). The sediments were mostly composed of quartz, carbonate minerals (calcite and dolomite), and feldspars. Minor or trace quantities of sulfate minerals or muscovite were present in some samples. The concentration of perchlorate associated with the sediments was estimated by sequential extractions with reagent grade water. Perchlorate concentrations ranged from non-detectable to approximately 750 μg/g. The perchlorate could be readily extracted with water and the concentration appeared to be independent of sediment characteristics and only dependent on the concentration of perchlorate in the pore water. Column experiments were conducted to estimate the retardation of perchlorate in several sediment samples, under saturated flow conditions. Bromide was used as a conservative tracer and the transport of perchlorate was modeled using the code CXTFIT. The column experiments suggest that perchlorate is a highly conservative tracer in these soils. Retardation factors ranged from 0.76 to 1.29. Flow interruption during the experiments suggests transport under equilibrium conditions, despite the high flowrate used in these experiments. Addition of zero valent iron to a sediment column did not affect perchlorate transport, under the experimental conditions studied.